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## **CLAIMS**

## What is claimed is:

- 1. A method of identifying an enzyme, the method comprising:
- (a) contacting a sample comprising an enzyme with a selected enzyme suicide substrate, wherein said contacting provides for covalent binding of the substrate to an amino acid of the enzyme to form a covalently modified enzyme; and
- (b) determining an amino acid sequence of at least a portion of the covalently modified enzyme, thereby identifying the enzyme.
  - 2. The method of claim 1, wherein the sample is a biological sample.
- 3. The method of claim 1, wherein the covalently modified enzyme is isolated before tandem mass spectrometry analysis.
- 4. The method of claim 3, wherein said selected enzyme substrate is radiolabeled.
- 5. The method of claim 3, wherein the covalently modified enzyme is isolated by one-dimensional isoelectric focusing.
- 6. The method of claim 3, wherein the covalently modified enzyme is isolated by two-dimensional gel electrophoresis.
- 7. The method of claim 3, wherein the covalently modified enzyme is isolated by fast protein liquid chromatography.
- 8. The method of claim 3, wherein the covalently modified enzyme is isolated by size-exclusion chromatography.
- 9. The method of claim 1, wherein the covalently modified enzyme is proteolytically cleaved with a first proteolytic enzyme before amino acid sequencing.

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10. The method of claim 9, wherein the covalently modified enzyme is proteolytically cleaved with a second proteolytic enzyme before amino acid sequencing.

- 11. The method of claim 1, wherein said enzyme is a terpene synthase, and wherein said selected enzyme substrate is a cyclopropyl-modified polyprenyl diphosphate.
- 12. The method of claim 11, wherein said cyclopropyl-modified polyprenyl diphosphate is selected from cyclopropylidene farnesyl diphosphate, cyclopropylidene geranyl diphosphate, cyclopropylidene geranylfarnesyl diphosphate, cyclopropylidene hexaprenyl diphosphate, cyclopropylidene heptaprenyl diphosphate, cyclopropylidene octaprenyl diphosphate, cyclopropylidene solanesyl diphosphate, cyclopropylidene decaprenyl diphosphate, cyclopropylidene undecaprenyl diphosphate, and cyclopropylidene dehydrodolichyl diphosphate.
- 13. The method of claim 1, wherein said enzyme is a terpene synthase, and wherein said selected enzyme substrate is a vinyl analog of a polyprenyl diphosphate.
- 14. The method of claim 13, wherein the vinyl analog is selected from 6-methylidene farnesyl diphosphate, 11-methylidene geranyl diphosphate, 16-methylidene geranylgeranyl diphosphate, 21-methylidene geranylfarnesyl diphosphate, 26-methylidene hexaprenyl diphosphate, 31-methylidene heptaprenyl diphosphate, 36-methylidene octaprenyl diphosphate, 41-methylidene solanesyl diphosphate, 46-methylidene decaprenyl diphosphate, and 51-methylidene undecaprenyl diphosphate.
- 15. The method of claim 1, wherein said amino acid sequence determination is by tandem mass spectrometry analysis.
- 16. The method of claim 1, wherein said amino acid sequence determination is by Edman degradation.
- 17. The method of claim 1, further comprising generating a nucleic acid having a degenerate nucleotide sequence encoding the amino acid sequence, wherein the nucleotide sequence is designed based on the amino acid sequence determined in step (b).

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18. The method of claim 17, wherein the nucleic acid is suitable for use as a hybridization probe to detect a nucleic acid that comprises a nucleotide sequence that encodes the enzyme.

19. The method of claim 17, wherein the nucleic acid is suitable for use to initiate synthesis of a nucleic acid amplification product by a DNA polymerase.